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(54) **Resin composition and mold made from such resin, for forming fibrous material**

Harzmischung und aus diesem Harz bestehendes Formwerkzeug zur Formung von faserartigem Material

Composition d'une résine et moule fait en cette résine pour le moulage de matériaux fibreux

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US-A- 5 296 335 US-A- 5 434 196

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Description

Field of the Invention

5 **[0001]** This invention relates to a radiation curable resin composition according to the precharacterising part of claim 1, to a process for the manufacture of a mold for making products from fibrous materials according to the precharacterising part of claim 13, a mold for making products from fibrous materials, (i.e. a mold for pulp molding) and a method for making products from fibrous materials.

10 Background of the Invention

15 **[0002]** Several methods are known to make products or articles from fibrous materials. One of these methods comprises the step of forming an article or a preform therefor, from pulp fiber with the use of a mold, which is also called pulp molding. Pulp molding is attracting increased attention from the point of view of resource saving and environmental protection by recycling, since various materials such as packaging materials can be made from used paper products.

20 **[0003]** In an example of the pulp molding process, a raw pulp suspension is prepared by dispersing pulp fibers in water to obtain a suspension and adding a thermosetting resin to the suspension to impregnate the pulp fibers with the thermosetting resin. Next, the method comprises a step in which the mold is contacted with the raw pulp suspension and the pressure is reduced inside the mold (metal mold). Since the mold is made so as to admit the passage of water from the raw pulp suspension, the pulp fibers accumulate over the surface of the mold. In this way a pulp fiber preform is formed which is then dried and subjected to pressure and/or elevated temperature to obtain the molded pulp product.

25 **[0004]** Figure 1 is a schematic sectional view of a mold used in pulp molding. In Figure 1, a mold 50 is a so-called draining mold. The mold 50 comprises a mold main body 58 in the shape of a hollow rectangular parallelepiped with a projection, which consists of three division molds (58A to 58C) each made from cast metal, and a lid 53 for closing an opening 52 of the mold main body 58.

30 **[0005]** The mold main body 58 (division molds 58A to 58C) has a plurality of suction holes 56 which provide communication between the inside space 51 and the outside of the mold. The outside surface of the mold main body 58 (division molds 58A to 58C) is covered with wire cloth 57A to 57C. The diameter of the suction holes 56 is within a range of about 2 to 15 mm. The size of the openings of the wire cloth 57A to 57C (size of the particles which can pass through the wire cloths) is within a range of about 0.1 to 1 mm.

35 **[0006]** A suction device 54 is connected to the mold 58 with a suction pipe 55. By operating the suction device 54, a reduced pressure is produced in the inside space 51 of the mold 58.

40 **[0007]** Figure 2 illustrates the process step in which the mold 50 is contacted with the pulp suspension to make a pulp fiber preform. In Figure 2, a raw pulp suspension 60, in which pulp fibers of a few millimeters in length are dispersed in water, is held in a raw material vat 59.

45 **[0008]** The main body 58 of the mold 50 is put in the raw pulp suspension 60. The suction device 54 is then operated to reduce the pressure of the inside space 51 of the mold main body 58. Because of this reduced pressure in the inside space 51, a suction force which attracts the pulp fibers is generated on the outside surface (the surface covered with the wire cloth 57A to 57C) of the mold main body 58. Being pulled by this force, the pulp fibers accumulate over the outside surface of the mold main body 58, and thereby the preform of the product is obtained. This preform is then subjected to several process steps such as drying and curing under pressure. Thereby, a molded product is obtained, which has a shape corresponding to that of the mold 50.

50 **[0009]** However, since the mold 50 shown in Figure 1 needs a wire mesh stretching operation to cover the outside surface of the mold main body 58 (division molds 58A to 58C) with the wire cloths 57A to 57C, it cannot be manufactured efficiently.

55 **[0010]** The wire mesh stretching operation is very difficult when stretching wire mesh along the surface of a mold which has complicated projections and recessions. Further, when the mold consists of two or more parts, each part needs a separate wire mesh stretching operation, making the wire mesh stretching operations still more complicated and difficult. The wire mesh stretching operation also requires skill in cutting and stretching the wire mesh. Furthermore, it is difficult to quickly meet a request for design change, because remake of the metal mold is required even for a partial change in the shape of the mold.

OBJECT OF THE PRESENT INVENTION

60 **[0011]** To solve the above problem, it can be considered to manufacture a mold using so-called "lamine fabricating" in which consecutive layers of a resin are irradiated with light to cure the resin (hereinafter referred to as light-irradiating lamine fabricating). For example, EP 0 732 181 describes a new molding tool with many suction holes using lamination molding techniques for molding a three dimensional shape product by subjecting material to be laminated to prescribed

treatment. US 5,296,335 describes a manufacturing method for a three-dimensional fiber reinforced part utilizing the single tool method of stereolithography.

Light-irradiating laminate fabricating is the method of forming a three-dimensional object composed of a plurality of firmly united superposed layers of cured resin by repeating the process of selectively irradiating a photocurable resin with light. For this light-irradiating laminate fabricating, conventional photocurable resins such as urethane acrylate, epoxy acrylate, a vinyl ether resin, and an epoxy resin can be used.

For example, US 5,434,196 discloses a resin composition for optical molding that comprises an epoxy acrylate resin, a free radical photo-initiator, a cationically polymerizable organic substance and a cationic photo-initiator. EP 0 535 828 discloses a method of generating three-dimensional objects by applying UV-light with a stereo-lithographic technique to a photopolymerizable resin composition comprising a compound having at least one polymerizable unsaturated bond per molecule (i.e. acrylate resins), a free radical photo-initiator, a cationic polymerizable compound, a cationic photo-initiator and a dye compound.

[0012] With the use of light-irradiating laminate fabricating, suction holes can be formed by aligning unexposed parts of all laminated resin layers so that when the uncured resin is removed continuous holes are apparent. It is therefore possible to form suction holes of any diameter by light-irradiating laminate fabricating. For example, suction holes with a diameter smaller than the length of the pulp fibers (1 mm or smaller, for example) can be easily formed. Suction holes with such a small diameter perform both the function of the suction holes 56 of the mold 50 shown in Figure 1, and that of the wire cloths 57A to 57C. Therefore, the wire mesh stretching operation which requires time and skill becomes unnecessary. Further, even a complicated-shape mold can be made in a single mold without dividing it. It was therefore expected that the manufacture of a mold for pulp molding would become more efficient, and a quicker response to requests for design change would become possible, by use of light-irradiating laminate fabricating.

[0013] However, the present inventors discovered, that there may be a problem with a mold for pulp molding which is made by some conventional light-irradiating laminate fabricating. That is, the cured resin from which the mold is made (cured resin obtained from the above photocurable resin composition) may not have adequate water-resisting capabilities, and the water in the raw pulp suspension permeates into the cured resin. Because of this water permeation, the strength of the mold gradually decreases, causing defects in the molded pulp product.

[0014] Forming a water-resistant coating layer over the surface of a mold made of cured resin in order to prevent water permeation is thought to be a possible method to solve the problem.

[0015] However, this method requires an additional coating process in the manufacturing of a mold for pulp molding, reducing the efficiency of manufacturing of a mold for pulp molding by light-irradiating laminate fabricating. In addition, the coating substance can fill the suction holes, making the mold defective.

[0016] This invention was made with the background as described above. The object of this invention is to provide a resin composition of which a fibrous material forming mold can be manufactured efficiently, which mold has good water-resistant properties (durability).

SUMMARY OF THE INVENTION

[0017] The above object is attained according to the invention by the radiation curable resin composition as defined in claim 1, by the process as defined in claim 13, by the mold as defined in claim 14 and by the method as defined in claim 17.

[0018] Particular embodiments of the invention are the subject of the respective dependent claims.

[0019] This resin composition of this invention is a radiation curable resin composition which upon cure has good water resistant properties. Preferably, the resin composition used for making a fibrous material forming mold by laminate fabricating is characterized in that the resin comprises a liquid constituent and a filler dispersed in the liquid, the liquid constituent comprises at least a photoreactive monomer and a photoreaction initiator.

[0020] Preferable constituents for the resin composition of this invention are as follows:

- (1) The filler is an inorganic substance.
- (2) The filler is in the form of spherical particles.
- (3) The filler content of the resin composition is 50 to 80 wt%, and preferably 50 to 70 wt%
- (4) An epoxy compound is used as the photoreactive monomer.
- (5) The resin composition comprises (A) a cationic polymerizable organic compound, (B) a cationic photopolymerization initiator, (C) an ethylenically unsaturated monomer, (D) a radical photopolymerization initiator, and (E) the filler.

[0021] The fibrous material forming mold of this invention is characterized in that it is obtained by repeating the process which selectively irradiates the resin composition of this invention with radiant energy to form a layer of cured resin.

[0022] The fibrous material forming mold of this invention is a mold used for molding fibrous material with a freeness value within the range of 400 to 600 ml and length of fibers within the range of about 0.3 to 3 mm. This mold preferably has suction holes 3 mm or smaller in diameter.

[0023] A mold (the fibrous material forming mold of this invention) with a plurality of suction holes of desired diameter (3.6 mm or smaller, for example) can be easily and efficiently manufactured by repeating the process which selectively irradiates a thin layer of the resin composition covering the previous layer with radiant energy to form a laminated layer of cured resin. Specifically, since the suction holes of the fibrous material forming mold of this invention perform both the function of the suction holes (producing a suction force which moves pulp fibers toward the surface of the mold) and that of the wire cloth (holding pulp fibers on the surface of the mold without admitting their passage) of a conventional draining mold, the wire mesh stretching operation which requires time and skill becomes unnecessary. A complicated-shape mold can be made in a single mold without it being divided. This enables a quicker response to requests for design changes.

[0024] The cured resin obtained from the resin composition of this invention appears to have high water-resistant properties. Therefore, a mold made of the cured resin obtained from the resin composition of this invention (fibrous material forming mold of this invention) retains the strength required for molding a fibrous material if put in a liquid with a fibrous material dispersed for a long time, and hence this mold can adequately endure repeated use over a long period.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] Figure 1 is a diagrammatic sectional view of a mold used for pulp molding.

[0026] Figure 2 is a diagram showing the use of the mold of Figure 1.

[0027] Figure 3 is an optical fabricating apparatus suited for manufacturing the fibrous materials forming mold of this invention.

[0028] Figure 4 is a perspective view of the fibrous materials forming mold of this invention.

[0029] Figure 5 is a partial sectional side view of the fibrous material forming mold shown in Figure 4.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

[0030] This invention is described in detail below.

Resin Composition

[0031] The resin composition of this invention is a radiation (hereinafter referred to as light or photo)-curable resin composition used for manufacturing a fibrous material forming mold by laminate fabricating using irradiation with light (hereinafter also referred to as optical fabricating). This resin composition contains a filler (solid component) dispersed in the liquid constituent comprising a photoreactive monomer, and a photoinitiator.

[0032] The resin composition of this invention preferably is a liquid composition which contains (E) a filler dispersed in the liquid constituent comprising (A) a cationic polymerizable organic compound, (B) a cationic photopolymerization initiator, (C) an ethylenically unsaturated monomer, and (D) a radical photopolymerization initiator. Hereinafter, the constituents of this resin composition are specifically described.

(A) Cationic polymerizable organic component

[0033] Cationic polymerizable organic component (hereinafter also referred to as the component (A)) as a constituent of the resin composition of this invention is an organic compound which polymerizes or cross-links in the presence of a cationic polymerization initiator when irradiated with light. Examples of such a cationic polymerizable organic compound, include epoxy compounds, oxetane compounds, oxolane compound, cyclic acetal compound, cyclic lactone compounds, thirane compounds, thietane compounds, vinyl ether compounds, spiro ortho ester compounds produced by the reaction of an epoxy compound and lactone, ethylenically unsaturated compounds, cyclic ether compounds, cyclic thioether compounds, vinyl compounds. Among these compounds, an epoxy compound is preferred because the curing rate of the prepared resin composition is high, and the cured resin obtained from the resin composition has good mechanical properties.

[0034] Epoxy compounds which can be used as the component (A) include bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol S diglycidyl ether, brominated bisphenol A diglycidyl ether, brominated bisphenol F diglycidyl ether, brominated bisphenol S diglycidyl ether, epoxy novolak resin, hydrogenated bisphenol A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, hydrogenated bisphenol S diglycidyl ether, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy) cyclohexane-metha-dioxane, bis(3,4-epoxycyclohexylmethyl) adipate, vinylcyclohexene oxide, 4-vinylepoxy cyclohex-

ane, bis(3,4-epoxy-6-methylcyclohexyl- methyl) adipate, 3,4-epoxy-6-methylcyclohexyl-3',4'-epoxy-6'-methyl cyclohexane carboxylate, methylenebis(3,4-epoxycyclohexane), dicyclopentadiene diepoxide, ethylene glycol di (3,4-epoxycyclohexylmethyl) ether, ethylene bis(3,4-epoxycyclohexanecarboxylate), epoxyhexahydrodioctyl phthalate, epoxyhexahydrophthalic acid di-2-ethylhexyl, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether; polyglycidyl ether of polyether polyol obtained by adding one or more kinds of alkylene oxide to an aliphatic polyhydric alcohol such as ethylene glycol, propylene glycol, and glycerol; diglycidyl ester of an aliphatic head chain dibasic acid; mono glycidyl ether of aliphatic higher alcohol; phenol, cresol, and butyl phenol and a monoglycidyl ether of the polyether alcohol obtained by adding an alkylene oxide to these; glycidyl ester of a higher fatty acid; epoxidated soybean oil, epoxy stearic acid butyl, epoxy stearic acid octyl, epoxidated linseed oil, and epoxidated polybutadiene, for example.

[0035] Among these compounds, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, hydrogenated bisphenol A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether,

3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate, bis(3,4-epoxycyclohexylmethyl) adipate, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, polyethylene glycol diglycidyl ether, and polypropylene glycol diglycidyl ether are preferred.

[0036] Epoxy compounds especially preferable as component (A) include those which have two or more alicyclic epoxy groups in one molecule, such as 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate, and bis (3,4-epoxycyclohexylmethyl) adipate. When this type of epoxy compound is present in an amount equal to or greater than 50 wt% in component (A), the polymerization rate (curing rate) of the prepared resin composition increases, and the time needed for laminate fabricating can be reduced. Further, the shrinkage upon cure of the three-dimensional product (mold) made of such a resin composition decreases, resulting in a smaller dimensional change of the mold over time.

[0037] Compounds other than epoxy compounds which can be used as component (A) include for example oxetane compounds such as trimethylene oxide, 3,3-dimethyl oxetane, 3,3-dichloro methyl oxetane, 3-ethyl-3-phenoxy methyl oxetane, and bis(3-ethyl-3-methyloxy) butane; oxolane compounds such as tetrahydrofuran and 2,3-dimethyl tetrahydrofuran; cyclic acetal compounds such as trioxane, 1,3-dioxolane, and 1,3,6-trioxane cyclooctane; cyclic lactone compounds such as β -propiolactone, ϵ -caprolactone; thiirane compounds such as ethylene sulfide, 1,2-propylene sulfide, and thioepichlorohydrin; thietane compounds such as 3,3-dimethylthietane; vinyl ether compound such as ethylene glycol divinyl ether, triethylene glycol divinyl ether, and trimethylolpropane trivinyl ether; spiro ortho-ester compounds obtained by the reaction of an epoxy compound and lactone; ethylenically unsaturated compounds such as vinyl cyclohexane, isobutylene, and polybutadiene; and derivatives of the above compounds.

[0038] Examples of commercially available cationic polymerizable organic compounds include UVR-6100, UVR-6105, UVR-6110, UVR-6128, UVR-6200, and UVR-6216 (Union Carbide Corp.); Celoxide 2021, Celoxide 2021P, Celoxide 2081, Celoxide 2083, Celoxide 2085, Celoxide 2000, Celoxide 3000, Glycidole, AOEX24, Cyclomer A200, Cyclomer M100, Epolead GT-300, Epolead GT-301, Epolead GT-302, Epolead GT-400, Epolead 401, and Epolead 403 (Daicel Co., Ltd.); Epicoat 828, Epicoat 812, Epicoat 1031, Epicoat 872, and Epicoat CT508 (Yuka Shell Company); KRM-2100, KRM-2110, KRM-2199, KRM-2400, KRM-2410, KRM-2408, KRM-2490, KRM-2200, KRM-2720, KRM-2750 (Asahi Denka Kogyo K.K.); Rapi-Cure DVE-3, CHVE, and PEPC (ISP Company); and VECTOMER 2010, 2020, 4010, and 4020 (Allied Signal Company).

[0039] The above cationic polymerizable compounds can be used singly or in combinations of two or more to prepare component (A).

[0040] The component (A) content of the liquid constituent of the resin composition of this invention is within the range of 30 to 95 wt%, preferably 40 to 90 wt%, and more preferably 50 to 85 wt%. If the amount of the component (A) is too small, the dimensional accuracy of the three-dimensional product (mold) made of the prepared resin composition can decrease. Further, the three-dimensional product (mold) is apt to deteriorate over time. If the amount of the component (A) is too large, the photocuring property of the resin prepared composition decreases, sometimes causing a decrease in efficiency of the laminate fabricating process.

(B) Cationic photopolymerization initiator

[0041] The cationic photopolymerization initiator (hereinafter also referred to as the component (B)) of the resin composition of this invention is a compound that can release a substance which initiates cationic polymerization of the above described component (A) when irradiated with for example UV or visible light. An especially preferable compound for the component (B) is as onium salt represented by the following general formula. This onium salt is a compound which releases a Lewis acid.



(In the above formula, the cation is onium; Z represents S, Se, Te, P, As, Sb, Bi, O, I, Br, Cl, or N≡N; and R¹, R², R³ and R⁴ represent the same or different organic acid. a, b, c, and d are each an integer from 0 to 3, (a+b+c+d) being equal to the valence of Z. M represents a metal or metalloid that is the central atom of the halide complex; B, P, As, Sb, Fe, Sn, Bi, Al, Ca, In, Ti, Zn, Sc, V, Cr, Mn, and Co, for example. X represents a halogen. m is the net electric charge of the halide complex ion. n is the number of halide atoms in the halide complex ion.

[0042] Examples of the anion (MX_n) in the above general formula include tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), hexafluoroantimonate (SbF₆⁻), hexafluoroarsenate (AsF₆⁻), and hexachloroantimonate (SbCl₆⁻).

[0043] In addition, onium salts having an anion represented by a general formula [MX_n(OH)⁻] can be used. Further, onium salts having other anions such as perchloric acid ion (ClO₄⁻), trifluoromethane sulfonic acid ion (CF₃SO₃⁻), fluorosulfone acid ion (FSO₃⁻), toluene sulfonic acid ion, trinitrobenzene sulfonic acid ion, and trinitrotoluene sulfonic acid ion can also be used.

[0044] Among these onium salts, an onium salt especially effective as the component (B) is an aromatic onium salt. Further, especially preferred onium salts include an aromatic halonium salt disclosed in Japanese Patent Applications Laid-Open No. 151996/1975, No. 158680/1975; VIA group aromatic onium salt disclosed in Japanese Patent Applications Laid-Open No. 151997/1975, No. 30899/1977, No. 55420/1981, and No. 125105/1980; VA group aromatic onium salt disclosed in Japanese Patent Application Laid-Open No. 158698/1975; oxosulfoxonium salt disclosed in Japanese Patent Applications Laid-Open No. 8428/1981, No. 149402/1981, and No. 192429/1982; aromatic diazonium salt disclosed in Japanese Patent Application Laid-Open No. 17040/1979; and thiopyrylium salt disclosed by USP No. 4,139,655. An Iron/allene complex and aluminum complex/photolysis silicon compound initiator can also be used.

[0045] Commercially available cationic photopolymerization initiators that can be preferably used as the component (B) include UVI-6950, UVI-6970, UVI-6974, and UVI-6990 (Union Carbide Corp.); Adekaoptomer SP-150, SP-151, SP-170, and SP-171 (Asahi Denka Kogyo K.K.); Irgacure 261 (Ciba Geigy); CI-2481, CI-2624, CI-2639, and CI-2064 (Nihon Soda Co., Ltd.); CD-1010, CD-1011, and CD-1012 (Satomer Co., Ltd.); DTS-102, DTS-103, NAT-103, NDS-103, TPS-103, MDS-103, MPI-103, and BBI-103 (Green Chemical Co., Ltd.). Among these, UVI-6970, UVI-6974, Adeka Optomer SP-170, SP-171, CD-1012, and MPI-103 are especially preferable, because they impart a high photocuring sensitivity to the prepared resin composition.

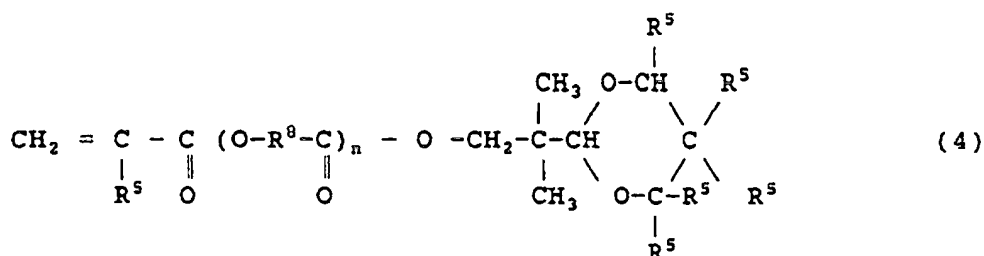
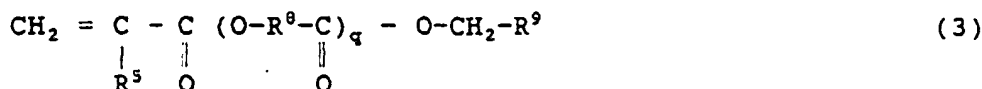
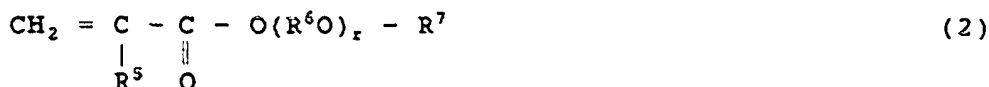
[0046] The above cationic photopolymerization initiators may be used singly or in combinations of two or more to prepare the component (B).

[0047] The component (B) content of the liquid constituent of the resin composition of this invention is within the range of 0.1 to 10 wt%, preferably 0.2 to 5 wt%, and more preferably 0.3 to 3 wt%. If the amount of the component (B) is too small, the photo-curing property of the prepared resin composition becomes too low, and the three-dimensional products (mold) made of the resin composition may not have adequate mechanical strength. If the amount of the component (B) is too large, the prepared resin composition does not have adequate light transparent properties required for the optical fabricating. As a result, mechanical strength such as the tenacity of the products (molds) made of the resin composition becomes too low.

(C) Ethylenically unsaturated monomer

[0048] The ethylenically unsaturated monomer (C) (herein referred to as the component (C)) of the resin composition of this invention is a compound which has one or more ethylenically unsaturated groups. Mono-functional monomers with one ethylenically unsaturated group in the molecule and poly-functional monomers with more than one ethylenically unsaturated group can be used as the component (C).

[0049] Mono-functional monomers which can be preferably used for the component (C) are acrylamide, (meth)acryloyl morpholine, 7-amino-3,7-dimethyloctyl (meth)acrylate, isobutoxymethyl (meth)acrylamide, isobornyloxyethyl (meth)acrylate, isobornyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, ethyldiethylene glycol (meth)acrylate, t-octyl (meth)acrylamide, diacetone (meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, lauryl (meth)acrylate, dicyclopentadiene (meth)acrylate, dicyclopentenloxyethyl (meth)acrylate, dicyclopentenyl (meth)acrylate, N,N-dimethyl (meth)acrylamide tetrachlorophenyl (meth)acrylate, 2-tetrachlorophenoxyethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, tetrabromophenyl (meth)acrylate, 2-tetrabromophenoxyethyl (meth)acrylate, 2-trichlorophenoxyethyl (meth)acrylate, tribromophenyl (meth)acrylate, 2-tribromophenoxyethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, vinyl caprolactam, N-vinyl pyrrolidone, phenoxyethyl (meth)acrylate, butoxyethyl (meth)acrylate, pentachlorophenyl (meth)acrylate, pentabromophenyl (meth)acrylate, polyethylene glycol mono (meth)acrylate, polypropylene glycol mono (meth)acrylate, bornyl (meth)acrylate, methyltriethylene diglycol (meth)acrylate, and the compounds represented by the following general formulas (2) to (4):



(In the above formulas, R⁵ represents a hydrogen atom or a methyl group. R⁶ represents an alkylene group with the number of carbon atoms within the range of 2 to 6, preferably 2 to 4. R⁷ represents a phenyl group, optionally substituted with an alkyl group with a number of carbons within the range of 1 to 12, preferably 1 to 9. R⁸ is an alkylene group with a number of carbons within the range of 2 to 8, preferably 2 to 5. r or n is an integer from 0 to 12, preferably 1 to 8. q is an integer from 1 to 8, preferably 1 to 4. R⁹ is a tetrahydrofuryl group.

[0050] Among these mono-functional monomers, isobornyl (meth)acrylate, lauryl (meth)acrylate, and phenoxyethyl (meth)acrylate are especially preferred.

[0051] Commercially available mono-functional monomers include Aronix M-101, M-102, M-111, M-113, M-117, M-152, and TO-1210 (Toagosei Chemical Industry Co., Ltd.), KAYARAD TC-110S, R-564, and R-128H (Nippon Kayaku Co., Ltd.), Viscoat 192, Viscoat 220, Viscoat 2311HP, Viscoat 2000, Viscoat 2100, Viscoat 2150, Viscoat 8F, and Viscoat 17F (Osaka Organic Chemical Industry, Ltd.).

[0052] Polyfunctional monomers which can be preferably used for the constituent (C) are ethylene glycol di(meth)acrylate, dicyclopentenyl di(meth)acrylate, triethylene glycol diacrylate, tetra ethylene glycol di(meth)acrylate, tricyclodecanediyl dimethylene di(meth)acrylate, tris(2-hydroxyethyl) isocyanurate di(meth)acrylate, tris(2-hydroxyethyl) isocyanurate tri(meth)acrylate, caprolactone-modified tris(2-hydroxyethyl) isocyanurate tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, ethylene oxide (hereinafter also referred to as EO for short)-modified trimethylolpropane tri(meth)acrylate, propylene oxide (hereinafter also referred to as PO for short)-modified trimethylolpropane tri(meth)acrylate, tripropylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, bisphenol A diglycidyl ether with (meth)acrylic acid adducts at both terminals, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, polyester di(meth)acrylate, polyethylene glycol di(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol tetra(meth)acrylate, caprolactone-modified dipentaerythritol hexa(meth)acrylate, caprolactone-modified dipentaerythritol penta(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, EO-modified bisphenol A di(meth)acrylate, PO-modified bisphenol A di(meth)acrylate, EO-modified hydrogenated bisphenol A di(meth)acrylate, PO-modified hydrogenated bisphenol A di(meth)acrylate, EO-modified bisphenol F di(meth)acrylate, and (meth)acrylate of phenol novolac polyglycidyl ether.

[0053] Commercially available polyfunctional monomers include SA1002 (Mitsubishi Chemical Corp.); Viscoat 195, Viscoat 230, Viscoat 260, Viscoat 215, Viscoat 310, Viscoat 214HP, Viscoat 295, Viscoat 300, Viscoat 360, Viscoat GPT, Viscoat 400, Viscoat 700, Viscoat 540, Viscoat 3000, and Viscoat 3700 (Osaka Organic Chemical Industry, Ltd.); KAYARAD R-526, HDDA, NPGDA, TPGDA, MANDA, R-551, R-712, R-604, R-684, PET-30, GPO-303, TMPTA, THE-330, DPHA, DPHA-2H, DPHA-2C, DPHA-2I, D-310, D-330, DPCA-20, DPCA-30, DPCA-60; DPCA-120, DN-0075, DN-2475, T-1420, T-2020, T-2040, TPA-320, TPA-330, RP-1040, RP-2040, R-011, R-300, and R-205 (Nippon Kayaku Co., Ltd.); Aronix M-210, M-220, M-233, M-240, M-215, M-305, M-309, M-310, M-315, M-325, M-400, M-6200, and M-6400 (Toagosei Chemical Industry Co., Ltd.); Light acrylate BP-4EA, BP-4PA, BP-2EA, BP-2PA, and DCP-A (Kyoe-

isya Chemical Co., Ltd.); New Frontier BPE-4, TEICA, BR-42M, and GX-8345 (Daiichi Kogyo Seiyaku Co., Ltd.), ASF-400 (Shin Nippon Steel Chemical Co., Ltd.); Repoxy SP-1506, SP-1507, SP-1509, VR-77, SP-4010, and SP-4060 (Showa Highpolymer Co., Ltd.); and NK ester A-BPE-4 (Shin-Nakamura Chemical Co., Ltd.).

[0054] The component (C) contains at least 60 wt% of a polyfunctional monomer having at least three ethylenically unsaturated bonds in the molecule. It is preferable to use component (C) in an amount of at least 70 wt.%, and more preferable, at least 80 wt.%. It is, however, especially preferred to use component (C) in an amount of about 100 wt.%. If component (C) substantially for 100 wt.% consists of one or more monomers containing three or more ethylenically groups, the photocuring property of the prepared resin composition increases, resulting in a decreased change over time of the three-dimensional products (molds) made of the resin composition.

[0055] A polyfunctional monomer having three or more functional monomers for this purpose can be selected from any of the above described tri(meth)acrylate compounds tetra(meth)acrylate compounds, penta(meth)acrylate compounds, and hexa(meth)acrylate compounds. Among them, trimethylolpropane tri(meth)acrylate, EO-modified trimethylolpropane tri(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, and ditrimethylolpropane tetra(meth)acrylate are especially preferable.

[0056] Monofunctional and polyfunctional monomers of component (C) may be used singly or in combinations of two or more, such that the amount of component (C) is preferably 7 to 25 wt%, and more preferably 10 to 20 wt%. If the amount of the component (C) is too small, the photocuring properties of the prepared resin composition becomes too low, and hence the three dimensional products (molds) made of the resin composition may not have adequate mechanical strength. On the other hand, if the amount of the component (C) is too large, the prepared resin composition does not have adequate light transmission properties required for light-irradiated laminate fabricating, and, as a result, the mechanical strength such as the tenacity of the three dimensional products (molds) made of the resin composition becomes too low.

(D) Radical photopolymerization initiator

[0057] The radical photopolymerization initiator (hereinafter also referred to as the component (D)) of the resin composition of this invention is a compound that decomposes by the action of radiation and initiates a radical polymerization reaction of the component (C) by the released radicals.

[0058] Radical photopolymerization initiators which can be used for the component (D) include ketophenone, acetophenone benzyl ketal, anthraquinone, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, carbazole, xanthone, 4-chlorobenzo-phenone, 4,4'-diaminobenzophenone, 1,1-dimethoxydeoxy-benzoin, 3,3'-dimethyl-4-methoxybenzophenone, thioxanethone compounds, 2-methyl-1-4-(methylthio) phenyl-2-morpholinopropan-2-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, triphenylamine, 2,4,6-trimethylbenzoyl diphenylphosphine oxides, bis(2,6-dimethoxybenzoyl)-2,4,4-tri-methylpentyl phosphine oxide, benzyl methyl ketal, 1-hydroxycyclohexyl-phenyl ketone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, fluorenone, fluorene, benzaldehyde, benzoin ethyl ether, benzoin propyl ether, benzophenone, Michler's ketone, 3-methylacetophenone, 3,3',4,4'-tetra(t-butylperoxycarbonyl) benzophenone (BTTB), and combination of BTTB and a color sensitizer such as xanthene, thioxanthene, cumarin, and ketocumarin, for example. Among these compounds, benzyl methyl ketal, 1-hydroxycyclohexylphenyl ketone, 2,4,6-trimethylbenzoyl diphenylphosphine oxides, and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one are especially preferable.

[0059] The above radical photopolymerization initiators may be used singly or in combinations of two or more.

[0060] The component (D) content of the liquid constituent of the resin composition of this invention is within the range of 0.01 to 10 wt% and preferably 0.1 to 8 wt%. If the amount of the component (D) is too small, the radical polymerization rate of the prepared resin composition (curing rate) becomes too low, and hence a longer time is required for laminate fabricating, or the dimensional accuracy decreases. On the other hand, if the amount of the component (D) is too large, the surplus amount of the radical photopolymerization initiator exerts a bad influence on the curing properties of the prepared resin composition and on the mechanical properties, heat resistance, and ease of handling.

(E) Filler

[0061] The filler (hereinafter also referred to as the component (E)) of the resin composition of this invention may be any substance without special limitation, but an inorganic substance is preferred from the point of view of the water-resisting capabilities and mechanical properties of the fibrous material forming molds made of the prepared resin composition.

[0062] Specifically, silica powder with an average particle size or fiber length of 1 to 50 μm , such as of fused silica and/or crystal silica is preferably used.

[0063] A filler, such as fused and/or crystal silica, of which the powder particles are spherical (0.9 or greater sphericity, for example) is especially preferred, because molds made of the prepared resin composition have good molding prop-

erties.

[0064] Sphericity, also known as the "degree of circularity", a ratio that measures the deviation of a spherical object from being a perfect sphere, and is defined by the formula 1. When the shape of a projected image is exactly spherical, the sphericity is defined as 1.

5

$$\text{Sphericity} = \frac{\sqrt[4]{4\pi S_p}}{C} = \frac{d_{pa}}{d_{pc}}$$

10 wherein S_p is a projection area, c is the peripheral length of the projected image, d_{pa} is the diameter of a circle having the same area as that of the projection area, and d_{pc} is the diameter of a circle having the same peripheral length as the projected image of the particle.

[0065] This sphericity can be measured using an image analyzer which can analyze a microphotograph taken by a scanning electron microscope (SEM). The average sphericity can be measured by calculating the average sphericity of 100 particles arbitrarily selected from a multitude of particles appearing in the microphotograph.

15 **[0066]** Commercially available silica powder products include Crystallite 3K-S, Crystallite NX-7, Crystallite MCC-4, Crystallite CMC-12, Crystallite A-1, Crystallite AA, Crystallite C, Crystallite D, Crystallite CMC-1, Crystallite C-66, Crystallite 5X, Crystallite A-2, Crystallite VX-S2, Crystallite VX-SR, Crystallite VX-X, Crystallite VX-S, HUSELEX RD-8, HUSELEX RD-120, HUSELEX MCF-4, HUSELEX GP-200T, HUSELEX ZA-30, HUSELEX RD-8, HUSELEX Y-40, HUSELEX E-2, HUSELEX Y-60, HUSELEX E-1, HUSELEX E-2, HUSELEX FF, HUSELEX X, HUSELEX ZA-20, IMSIL A-25, IMSIL A-15, IMSIL A-10, and IMSIL A-8 (Ryushin Co., Ltd.); SUNSPHERE H-31, SUNSPHERE H-32, SUNSPHERE H-51, SUNSPHERE H-52, SUNSPHERE H-121, SUNSPHERE H-122, SUNSPHERE L-31, SUNSPHERE L-51, SUNSPHERE L-121, SUNSPHERE NP-30, SUNSPHERE NP-100, and SUNSPHERE NP-200 (Asahi Glass Co., Ltd.); Silstar MK-08 and MK-15 (Nippon Chemical Industrial Co., Ltd.); FB-48 (Denki Kagaku Kogyo K.K.); Nipsil SS-10, Nipsil SS-15, Nipsil SS-10A, Nipsil SS-20, Nipsil SS-30P, Nipsil SS-30S, Nipsil SS-40, Nipsil SS-50, Nipsil SS-50A, Nipsil SS-70, Nipsil SS-100, Nipsil SS-10F, Nipsil SS-50F, Nipsil SS-50B, Nipsil SS-50C, Nipsil SS-72F, Nipsil SS-170X, Nipsil SS-178B, Nipsil E-150K, Nipsil E-150J, Nipsil E-1030, Nipsil ST-4, Nipsil E-170, Nipsil E-200, Nipsil E-220, Nipsil E-200A, Nipsil E-1009, Nipsil E-220A, Nipsil E-1011, Nipsil E-K300, Nipsil HD, Nipsil HD-2, Nipsil N-300A, Nipsil L-250, Nipsil G-300, Nipsil E-75, Nipsil E-743, and Nipsil E-74P (Nippon Silica Industry, Ltd.), for example.

30 **[0067]** Inorganic filler substances other than silica powder include, glass powder, alumina, alumina hydrate, magnesium oxide, magnesium hydroxide, barium sulfate, calcium sulfate, calcium carbonate, magnesium carbonate, silicate mineral, diatomaceous earth, silica sand, silica powder, oxidation titanium, aluminum powder, bronze, zinc powder, copper powder, lead powder, gold powder, silver dust, glass fiber, titanite acid potassium whiskers, carbon whiskers, sapphire whiskers, verification rear whiskers, boron carbide whiskers, silicon carbide whiskers, and silicon nitride whiskers.

35 **[0068]** Commercially available inorganic filler products include Glass bead GB210, GB210A, GB210B, GB210C, GB045Z, GB045ZA, GB045ZB, GB045ZC, GB731, GB731A, GB731B, GB731C, GB731M, GB301S, EGB210, EGB210A, EGB210B, EGB210C, EGB045Z, EGB045ZA, EGB045ZB, EGB045ZC, MB-10, MB-20, EMB-10, EMB-20, HSC-070Q, HSC-024X, HSC-080S, HSC-070G, HSC-075L, HSC-110, HSC-110A, HSC-110B, and HSC-110C (Toshiba Balotini Co., Ltd.); Radiolite #100, Radiolite Fine Flow B, Radiolite Fine Flow A, Radiolite Sparkle Flow, Radiolite Special Flow, Radiolite #300, Radiolite #200, Radiolite Clear Flow, Radiolite #500, Radiolite #600, Radiolite #2000, Radiolite #700, Radiolite #500S, Radiolite #800, Radiolite #900, Radiolite #800S, Radiolite #3000, Radiolite Ace, Radiolite Suprace, Radiolite High Ace, Radiolite PC-1, Radiolite Delux P-5, Radiolite Delux W-50, Radiolite Microfine, Radiolite F, Radiolite SPF, Radiolite GC, Topco #31, Topco #34, Topco #36, Topco #38, and Topco #54 (Showa Chemical Industry Co., Ltd.); Higilite H-X, Higilite H-21, Higilite H-31, Higilite H-32, Higilite H-42, Higilite H-42M, Higilite H-43, Higilite H-32ST, Higilite H-42STV, Higilite H-42T, Higilite H-34, Higilite H-34HL, Higilite H-32I, Higilite H-42I, Higilite H-42S, Higilite H-210, Higilite H-310, Higilite H-320, Higilite H-141, Higilite H-241, Higilite H-341, Higilite H-320I, Higilite H-320ST, Higilite HS-310, Higilite HS-320, Higilite HS-341, Alumina A-42-6, alumina A-42-1, Alumina A-42-2, Alumina A-42-3, Alumina A-420, Alumina A-43-M, Alumina A-43-L, Alumina A-50-K, Alumina A-50-N, Alumina A-50-F, Alumina AL-45-H, Alumina AL-45-2, Alumina AL-45-1, Alumina AL-43-M, Alumina AL-43-L, Alumina AL-43PC, Alumina AL-150SG, Alumina AL-170, Alumina A-172, Alumina A-173, Alumina AS-10, Alumina AS-20, Alumina AS-30, Alumina AS-40, and Alumina AS-50 (Showa Denko K.K.); Starmague U, Starmague M, Starmague L, Starmague P, Starmague C, Starmague CX, High purity magnesia HP-10, High purity magnesia HP-10N, High purity magnesia HP-30, Star brand-200, Star brand-10, Star brand-10A, Star brand magnesium carbonate Venus, Star brand magnesium carbonate two stars, Star brand magnesium carbonate one star, Star brand magnesium carbonate S, Star brand magnesium carbonate Fodder, Star brand heavy magnesium carbonate, High purity magnesium carbonate GP-10, High purity magnesium carbonate 30, Star brand light calcium carbonate general use, Star brand light calcium carbonate EC, and Star brand light calcium carbonate KFW-200 (Konoshima Chemical Industry Co., Ltd.); MKC Silica

GS50Z and MKC Silica SS-15 (Mitsubishi Chemical Corp.), Admafine SO-E3, Admafine SO-C3, Admafine AO-800, Admafine AO-809, Admafine AO-500, and Admafine AO-509 (Adomatex Co., Ltd.); M. S. GEL D-5-60A, M. S. GEL D-5-120A, M. S. GEL D-5-300A, M. S. GEL D-20-60A, M. S. GEL D-20-120A, M. S. GEL D-20-300A, SILDEX H-31, SILDEX H-32, SILDEX H-51, SILDEX H-52, SILDEX H-121, SILDEX H-122, SILDEX L-31, SILDEX L-51, SILDEX L-121, SILDEX F-51, and SILDEX F-121 (Asahi Glass); SYLYSIA 250, SYLYSIA 250N, SYLYSIA 256, SYLYSIA 256N, SYLYSIA 310, SYLYSIA 320, SYLYSIA 350, SYLYSIA 358, SYLYSIA 430, SYLYSIA 431, SYLYSIA 440, SYLYSIA 450, SYLYSIA 470, SYLYSIA 435, SYLYSIA 445, SYLYSIA 436, SYLYSIA 446, SYLYSIA 456, SYLYSIA 530, SYLYSIA 540, SYLYSIA 550, SYLYSIA 730, SYLYSIA 740, SYLYSIA 770, SYLOPHOBIC100, and SYLOPHOBIC 200 (Fuji Silysia Chemical Co., Ltd.); and Tismo-D, Tismo-L, Tofica Y, Tofica YN, Tofica YB, Dendol WK-200, Dendol WK-200B, Dendol WK-300, Dendol BK-200, Dendol BK-300, Swanite, and Barihigh B Super Dendol (Otsuka Chemical Co., Ltd.).

[0069] The condition of the surface of the particles of the filler used and the impurities contained in filler from the manufacturing process can affect the curing reaction of the resin composition. In such cases, it is preferable to wash the filler particles or coat the particles with an appropriate primer as a method of improving the curing properties.

[0070] These inorganic fillers may also be surface-treated with a silane coupling agent. Silane coupling agents which can be used for this purpose include vinyl trichlorosilane, vinyl tris (β -methoxyethoxy) silane, vinyltriethoxy silane, vinyltrimethoxy silane, γ -(methacryloxypropyl)trimethoxy silane, β -(3,4-epoxycyclohexyl)ethyltrimethoxy silane, γ -glycidoxypolytrimethoxy silane, γ -glycidoxypolydimethyl diethoxy silane, N- β -(aminoethyl)- γ -aminopropyltrimethoxy silane, N- β -(aminoethyl)- γ -aminopropylmethyldimethoxy silane, γ -aminopropyltriethoxysilane, N-phenyl- γ -amino propyl trimethoxy silane, γ -mercaptopropyl trimethoxysilane, and γ -chloropropyltrimethoxy silane.

[0071] The above inorganic fillers may be used singly or in combination of two or more to make up the component (E). By using inorganic fillers with different properties in combination, it is possible to impart the desirable properties derived from the fillers to the prepared resin composition. Further, the prepared resin composition can have a remarkably different fluidity if the grain size or fiber length distribution of the inorganic filler used is different, though the substance, the average grain size or fiber length, and the amount are the same. Therefore, by appropriately determining not only the average grain size or fiber length but also the grain size or fiber length distribution, or by using inorganic fillers of the same substance with different average grain sizes or fiber lengths in combination, the necessary amount of the filler and the fluidity and other properties of the prepared resin can be controlled as desired.

[0072] The component (E) content of the resin composition of this invention is within the range of 30 to 80 wt% and more preferably 50 to 70 wt% of the total composition. If the amount of the component (E) is too small, the water-resistant properties and the durability of the molds made of the prepared resin composition do not increase sufficiently. Further, the viscosity of the prepared resin composition becomes too low, causing precipitation of the filler. On the other hand, if the amount of the component (E) is too large, the fluidity of the prepared resin composition becomes too low, rendering the resin composition difficult to handle. The excessive amount of the component (E) can also affect the time needed for laminate fabricating of the resin composition, causing the time to increase.

[0073] Organic fillers which can be used for the component (E) are high cross-linked organic substances such as rubber and resin.

Optional constituents and additives

[0074] The resin composition of this invention may contain optional constituents other than the constituents (A) to (E) described above, within the limits that do not impair the photo-curing properties of the resin composition. The optional constituents include photosensitizer (polymerization promoters) consisting of amine compounds such as triethanolamine, methyl diethanolamine, triethylamine, and diethylamine; photosensitizers consisting of thioxanethone, derivatives of thioxanethone, anthraquinone, derivatives of anthraquinone, anthracene, derivatives of anthracene, perylene, derivatives of perylene, benzophenone, benzoin isopropyl ether; and reactive diluents such as vinyl ether, vinyl sulfide, vinyl urethane, urethane acrylate, and vinyl urea, for example.

[0075] The resin composition of this invention may also contain various kinds of additives. Examples of suitable additives include resins or polymers such as epoxy resin, polyamide, polyamideimide, polyurethane, polybutadiene, polychloroprene, polyether, polyester, styrene/butadiene styrene block copolymer, petroleum resin, xylene resin, ketone resin, cellulose resin, fluorine containing oligomer, and silicon containing oligomer; polymerization inhibitors such as for example phenothiazine, and 2,6-di-*t*-butyl-4-methyl phenol; polymerization initiation assistants, leveling agents, wettability improvers, surfactants, plasticizers, UV absorbers, silane coupling agents, resin particles, pigment, and dyes.

[0076] The resin composition of this invention is prepared by mixing the above described components (A) to (D), optional constituents, and additives into a homogenous resin solution (liquid constituent) and then dispersing the component (E) in the liquid constituent.

[0077] The viscosity (at 25°C) of the thus-prepared resin composition is preferably within the range of 500 to 20,000 cps, and more preferably within the range of 2,000 to 8,000 cps.

Fibrous material forming mold

[0078] The resin composition of this invention is suited as a photocurable resin composition used for manufacturing fibrous material forming molds by optical fabricating. A fibrous material forming mold, made of laminated layers of cured resin in a desired shape, can be formed of the resin composition of this invention by repeating the process which selectively irradiates a thin layer of the resin composition overlaid on the previous layer with radiant energy such as visible light, ultraviolet light, and infrared light.

[0079] Specifically, the resin composition of this invention is supplied on an appropriate supporting stage to form a thin layer (1) of the resin composition over the stage. The thin layer (1) is selectively irradiated with light, and becomes a solid cured resin layer (1). Next, the resin composition is supplied on the cured resin layer (1) to form a thin layer (2) of the resin composition over the cured resin layer (1). The thin layer (2) of the resin composition is then selectively irradiated with light, and becomes a cured resin layer (2) which is superposed on and firmly united with the cured resin layer (1). By repeating this process, changing or not changing the pattern of light irradiation, a fibrous material forming mold in a three-dimensional shape is formed of a plurality of cured resin layers which are united into a solid body.

[0080] With the use of this optical fabricating method, suction holes can be formed by aligning the unexposed parts of all laminated layers so that the uncured resin can be removed so continuous holes are formed. Since suction holes are formed in this manner by the optical fabricating method, the diameter and pitch of the suction holes can be freely selected as desired. For example, suction holes with a diameter smaller than the length of the pulp fibers (1 mm or smaller in diameter, for example) can be easily formed.

[0081] There are no particular requirements for the means for selectively irradiating the resin composition of this invention with radiation. Various means can be used. For example, (1) a means which selectively irradiates the resin composition with light by scanning with a laser light beam or light beam focused with lenses and mirrors, with the light being switched on and off, (2) a means which selectively irradiates the resin composition with non-convergent light through a mask with a pattern of transparent parts predetermined for each layer, and (3) a means which selectively irradiates the resin composition with light beams transmitted through a light guiding means consisting of a large number of bundled optical fibers. For the means which selectively irradiates the resin composition with non-convergent light through a mask, a liquid-crystal shutter device, each element area of which can be selectively switched between the opaque and transparent states, can be used. When the mold to make has a complicated shape or require a high dimensional accuracy, a irradiating means using a scanning laser light beam is preferable.

[0082] Figure 3 is a schematic diagram of the structure of an optical fabricating apparatus which is suited for manufacturing the fibrous material forming mold of this invention. An optical fabricating apparatus 1 comprises a computing means 2, a control means 3, a light beam scanning means 4, a moving mechanism 5, a light source 6, and a resin liquid vessel 7.

[0083] The computing means 2 generates control information such as contour section data and other manufacturing parameter data from the shape of the mold and the properties of the resin composition used. Control information is sent to the control means 3, and the control means 3 controls the light beam scanning means 4 and the moving mechanism 5. The light beam scanning means 4 scans a light beam L from the light source 6 such as an argon laser over the desired region of the surface 8a of the resin composition 8 held in the resin liquid vessel 7 under the control of the control means 3. The moving mechanism 5 lowers the stage 14 by a predetermined distance each time a layer of cured resin is formed.

[0084] With the use of this optical fabricating apparatus 1, a three dimensional object (fibrous material forming mold of this invention) can be formed in the resin liquid vessel 7 by repeating the process which cures the thin layer of the resin composition 8 at the surface 8a in a required two-dimensional shape and the operation which lowers the stage 14 by the moving mechanism 14 by a predetermined step.

[0085] The thus-obtained fibrous material forming mold is next subjected to a process which removes the unexposed resin composition remaining on the surface, and is then subjected to a washing process as necessary. For this washing, organic solvents represented by alcohol such as isopropyl alcohol and ethyl alcohol, esters such as ethyl acetate, and ketones such as acetone and methyl ether, aliphatic system organic solvents represented by terpene and glycol ester, a low-viscosity thermosetting resin composition, and an photocurable resin composition can be used as the washing agent.

[0086] To obtain a fibrous material forming mold with a smoother surface, it is preferable to post-cure the mold by heat treatment or light irradiation according to the type of resin composition used after the above washing. This post-curing process can cure not only the resin composition on the surface of the mold, but also the uncured resin composition remaining inside the mold. It is therefore preferable to perform the post-curing process after washing with an organic solvent.

[0087] Figure 4 is a perspective view of an example of the fibrous material forming mold of this invention. Figure 5 is a partial sectional side view of the fibrous material forming mold shown in Figure 4. In Figures 4 and 5, 21 indicates the mold main body, 22 the lid, 23 the inside space, 24A the vertical molding surface, 24B the horizontal molding

surface, and 25 suction holes by which the inside space 23 communicates with the outside.

[0088] The fibrous material forming mold shown in Figures 4 and 5 is a mold for forming a fibrous material with a freeness value within the range of 400 to 600 ml and a fiber length within the range of about 0.3 to 3 mm (pulp fibers, plant fibers, metal fibers, and so on), for example.

5 [0089] Here, the freeness value is a numerical value indicating water drainability (a measure of the ease of water drain from fibers) that is measured according to the method specified by JIS P 8121, TAP PI T227, ISO 5267/1~2, and SCAN M3 and 4.

[0090] The diameter of the suction holes in the vertical molding surface 24A is preferably 3.6 mm or smaller, and more preferably 0.3 to 1.4 mm. The diameter of the suction holes in the horizontal molding surface 24B is preferably 10 3.0 mm or smaller, and more preferably 0.3 to 1.2 mm.

Example

[0091] An example of this invention is described below.

15

Example 1

(1) Resin composition preparation:

20 [0092] A homogeneous resin solution (liquid constituent) was prepared by mixing the following compounds and agitating the mixture for two hours at 40°C:

- 3,4-Epoxy cyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (component (A): UVR-6110, manufactured by Union Carbide Corp.) 23.0 parts by weight
- 25 - Butanediol diglycidyl ether (component (A): Araldite DY-220, manufactured by Ciba Geigy) 8.6 parts by weight
- Triaryl sulfonium hexafluoroantimonate photopolymerization initiator (component (B): SP-171, manufactured by Asahi Denka Kogyo K.K.) 0.95 parts by weight
- Trimethylolpropane triacrylate (component (C): VISCOAT-295, manufactured by Osaka Organic Chemical Ind. Co., Ltd.) 3.9 parts by weight
- 30 - Dipentaerythritol hexacrylate (component (C): KAYARAD DPHA, manufactured by Nippon Kayaku Co., Ltd.) 2.4 parts by weight
- 1-Hydroxycyclohexylphenyl ketone (component (D): Irgacurel84, manufactured by Ciba Geigy) 0.95 parts by weight
- 35 - β -(3,4-Epoxy cyclohexyl)ethyltrimethoxy silane (silane coupling agent: Silace S530 (manufactured by Chisso Corp.) 0.60 parts by weight

[0093] Next, 59.6 parts by weight of silica beads (component (E), SUNSPHERE NP-100 (manufactured by Ashahi Glass Co., Ltd.) was added to the resin solution and dispersed in the solution using a homogenizer at room temperature. The resin composition of this invention was thus prepared. In this process, the surface of the silica beads was treated 40 with β -(3,4-epoxycyclohexyl)ethyltrimethoxy silane simultaneously. The viscosity of the resin composition was measured as 4,800 cps (at 25°C). A test sample was made by curing the resin composition, and the Young's modulus was measured. The Young's modulus was 710 kg/mm².

45 (2) Mold formation

[0094] The fibrous material forming mold of this invention in the shape shown in Figures 4 and 5 was formed of the resin composition (filler content: 59.6 wt%) prepared in the above step (1) with the use of an optical fabricating apparatus SOLID CREATOR JSC-2000 (manufactured by Sony Corporation) shown in Figure 3. The diameter of the suction holes open in the vertical forming surface 24A was 0.8 mm, and that of the suction holes open in the horizontal forming surface 24B was 0.5 mm. 50

(3) Test of the mold

45 [0095] Preforming of pulp fibers was conducted 100,000 times consecutively by means of the fibrous material forming mold formed in step (2). The freeness value of the pulp fibers in the raw pulp suspension in which the mold was placed was within the range of 400 to 600 ml, and the length of the pulp fibers was within the range of 2 to 3 mm. Preforms of pulp fibers were inspected after 100,000 preform operations, and no problem was found with the preforms. There was also no decrease in strength of the mold caused by absorption of water.

Example for comparison

[0096] A resin composition for comparison, which was composed of only the resin solution (liquid constituent), was prepared in the same manner as step (1) of Example 1 except that the silane coupling agent was not used and the silica beads were not dispersed in the composition.

[0097] Next, a fibrous material forming mold was formed of the resin composition in the same manner as in step (2) of Example 1. Then, preforming of pulp fibers was repeated in the same manner as in step (3) of Example 1. A degradation, specifically decrease of dimensional accuracy, was found in the 30th preform. A decrease in strength of the mold caused by absorption of water also occurred, and the mold broke during the 45th preform.

[0098] With the use of the resin composition of this invention, it becomes possible to manufacture a fibrous material forming mold having a large number of suction holes of a desired diameter easily and efficiently. It also becomes possible to quickly respond to a design change and an additional order.

[0099] Further, since the fibrous material forming mold of this invention is made of a cured resin with high water-resistant properties, the decrease in strength of the mold caused by absorption of water is small if the mold is placed in the raw pulp suspension for a long time. Therefore, the mold has high durability with which it can endure repeated use over a long time.

Claims

1. A radiation curable resin composition comprising at least a liquid constituent and a filler wherein the liquid constituent comprises at least one photoreaction monomer and at least one photoinitiator, **characterized in that** the radiation curable resin composition comprises 50 to 80 wt.% of a filler, based on the total weight of the composition.

2. The radiation curable resin composition, according to claim 1, wherein the liquid constituent of the resin composition is formulated from components comprising:

- (A) 30-95 wt.% of a cationic polymerizable compound:
- (B) 0.1-10 wt.% of a cationic photopolymerization initiator
- (C) 5-30 wt.% of an ethylenically unsaturated monomer
- (D) 0.01-10 wt.% of a radical photopolymerization initiator

wherein the amounts of the components of the liquid constituent of the composition add up to 100 wt.%.

3. The radiation curable resin composition, according to any one of claims 1-2, wherein the liquid constituent comprises a cationic polymerizable compound composed of 50 wt% or more of an epoxy containing compound.

4. The radiation curable resin composition, according to any one of claims 1-3, wherein the liquid constituent comprises a cationic polymerizable compound composed of 50 wt% or more of an epoxy compound selected from the group 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate and bis (3,4-epoxycyclohexylmethyl)adipate.

5. The radiation curable resin composition, according to any one of claims 1-4, wherein the liquid constituent comprises an ethylenically unsaturated monomer component comprising at least 60 wt% of a polyfunctional monomer having at least three ethylenically unsaturated bonds in the molecule.

6. The radiation curable resin composition, according to any one of claims 1-5, wherein said filler is selected from the group of organic fillers, inorganic fillers or a mixture of inorganic and organic fillers.

7. The radiation curable resin composition, according to any one of claims 1-5, wherein the filler is an organic compound selected from the group of resin(s), rubber(s), or a mixture of resin(s) and rubber(s).

8. The radiation curable resin composition, according to any one of claims 1-6, wherein said filler is a powder having spherical particles.

9. The radiation curable resin composition, according to any one of claims 1-6,
wherein the inorganic filler is selected from the group of fused silica, crystal silica or a mixture of fused silica and
crystal silica.
10. The radiation curable resin composition, according to any one of claims 1-5,
wherein said filler is a silica powder having an average particle size or fiber length of 1 to 50 µm.
11. The radiation curable resin composition, according to any one of claims 9-10,
wherein said filler is treated with a silane coupling agent.
12. The radiation curable resin composition, according to any one of claims 9-11,
wherein said composition further comprises a silane coupling agent.
13. Process for the manufacture of a mold for making products from fibrous materials by performing a combination of
steps of
 - (1) applying a thin layer of a radiation curable resin composition on a supporting stage
 - (2) selectively irradiating the thin layer of resin as to cure a selected part of said resin
 - (3) applying a further thin layer of resin,and repeating steps (2) and (3) as to obtain a three dimensional shape of a plurality of cured layers, **characterized
in that** the resin composition, as defined in any one of claims 1-12, is used.
14. Mold for making products from fibrous materials, obtainable by a process according to claim 13.
15. Mold according to claim 14, wherein the mold contains suction holes with a diameter of less than 3.6 mm.
16. Mold according to any one of claims 14-15, wherein the mold has a freeness value of about 400-600 ml (according
to JIS 8121).
17. Method for making products from fibrous materials by using a mold according to any one of claims 13-16, in which
the mold is contacted with a raw pulp suspension, reducing the pressure inside the mold to make a pulp-fiber
preform which is then dried and optionally cured as to obtain a molded pulp product

Patentansprüche

1. Durch Strahlung härtbare Harzzusammensetzung, umfassend mindestens einen flüssigen Bestandteil und ein
Füllmittel, wobei der flüssige Bestandteil mindestens ein Photoreaktionsmonomer und mindestens einen Photo-
initiator umfaßt, **dadurch gekennzeichnet, daß** die durch Strahlung härtbare Harzzusammensetzung 50 bis 80
Gew.-% eines Füllmittels, basierend auf dem Gesamtgewicht der Zusammensetzung, umfaßt.
2. Durch Strahlung härtbare Harzzusammensetzung nach Anspruch 1, wobei der flüssige Bestandteil der Harzzu-
sammensetzung aus Komponenten formuliert ist, umfassend:
 - (A) 30-95 Gew.-% einer kationischen polymerisierbaren Verbindung
 - (B) 0,1-10 Gew.-% eines kationischen Photopolymerisationsinitiators
 - (C) 5-30 Gew.-% eines ethylenisch ungesättigten Monomers
 - (D) 0,01-10 Gew.-% eines radikalischen Photopolymerisationsinitiators,wobei sich die Mengen der Komponenten des flüssigen Bestandteils der Zusammensetzung auf 100 Gew.-%
addieren.
3. Durch Strahlung härtbare Harzzusammensetzung nach einem der Ansprüche 1-2, wobei der flüssige Bestandteil
eine kationisch polymerisierbare Verbindung umfaßt, die 50 Gew.-% oder mehr einer Epoxy-enthaltenden Verbin-
dung umfaßt.
4. Durch Strahlung härtbare Harzzusammensetzung nach einem der Ansprüche 1 bis 3, wobei der flüssige Bestand-

teil eine kationische polymerisierbare Verbindung umfaßt, die 50 Gew.-% oder mehr einer Epoxyverbindung umfaßt, ausgewählt aus der Gruppe 3,4-Epoxy-cyclohexylmethyl-3',4'-epoxycyclohexancarboxylat und Bis(3,4-epoxy-cyclohexylmethyl)adipat.

- 5 5. Durch Strahlung härtbare Harzzusammensetzung nach einem der Ansprüche 1 bis 4, wobei der flüssige Bestandteil eine ethylenisch ungesättigte Monomerkomponente umfaßt, welche mindestens 60 Gew.-% eines polyfunktionalen Monomers mit mindestens drei ethylenisch ungesättigten Bindungen in dem Molekül umfaßt.
- 10 6. Durch Strahlung härtbare Harzzusammensetzung nach einem der Ansprüche 1 bis 5, wobei das Füllmittel ausgewählt ist aus der Gruppe organischer Füllmittel, anorganischer Füllmittel oder einem Gemisch von anorganischen und organischen Füllmitteln.
- 15 7. Durch Strahlung härtbare Harzzusammensetzung nach einem der Ansprüche 1 bis 5, wobei das Füllmittel eine organische Verbindung ist, ausgewählt aus der Gruppe von Harz(en), Kautschuk(en) oder einem Gemisch von Harz(en) und Kautschuk(en).
- 20 8. Durch Strahlung härtbare Harzzusammensetzung nach einem der Ansprüche 1 bis 6, wobei das Füllmittel ein Pulver mit kugelförmigen Teilchen ist.
- 25 9. Durch Strahlung härtbare Harzzusammensetzung nach einem der Ansprüche 1 bis 6, wobei das anorganische Füllmittel ausgewählt ist aus der Gruppe von hochdisperser Kieselsäure, kristallinem Siliziumdioxid oder einem Gemisch von hochdisperser Kieselsäure und kristallinem Siliziumdioxid.
- 30 10. Durch Strahlung härtbare Harzzusammensetzung nach einem der Ansprüche 1 bis 5, wobei das Füllmittel ein Siliziumdioxidpulver mit einer durchschnittlichen Teilchengröße oder Faserlänge von 1 bis 50 µm ist.
- 35 11. Durch Strahlung härtbare Harzzusammensetzung nach einem der Ansprüche 9 bis 10, wobei das Füllmittel mit einem Silan-Kupplungsmittel behandelt ist.
- 40 12. Durch Strahlung härtbare Zusammensetzung nach einem der Ansprüche 9 bis 11, wobei die Zusammensetzung weiter ein Silankupplungsmittel umfaßt.
- 45 13. Verfahren zur Herstellung einer Form zum Herstellen von Produkten aus faserhaltigen Materialien durch Durchführen einer Kombination von Schritten
 - (1) Aufbringen einer dünnen, durch Strahlung härtbaren Zusammensetzung auf einen tragenden Zustand
 - (2) selektives Bestrahlen der dünnen Schicht aus Harz, um einen ausgewählten Teil des Harzes zu härten
 - (3) Aufbringen einer weiteren dünnen Schicht aus Harz,
- 50 und Wiederholen der Schritte (2) und (3), um so eine dreidimensionale Form aus einer Vielzahl von gehärteten Schichten zu erhalten, **dadurch gekennzeichnet, daß** die Harzzusammensetzung, wie in einem der Ansprüche 1 bis 12 definiert, verwendet wird.
- 55 14. Form zur Herstellung von Produkten aus faserartigen Materialien, erhältlich durch ein Verfahren nach Anspruch 13.
15. Form nach Anspruch 14, wobei die Form Sauglöcher mit einem Durchmesser von weniger als 3,6 mm enthält.
16. Form nach einem der Ansprüche 14-15, wobei die Form eine Stoffdurchlässigkeit (freeness value) von etwa 400-600 ml (gemäß JIS 8121) aufweist.
17. Verfahren zur Herstellung von Produkten aus faserartigen Materialien unter Verwendung einer Form gemäß einem der Ansprüche 13-16, wobei die Form in Kontakt mit einer Rohzellstoff-Suspension gebracht wird, der Druck innerhalb der Form vermindert wird, um eine Zellstoffaservorform herzustellen, welche anschließend getrocknet und gegebenenfalls gehärtet wird, um so ein geformtes Zellstoffprodukt zu erhalten.

Revendications

1. Composition de résine durcissable par rayonnement comprenant au moins un constituant liquide et une charge, dans laquelle le constituant liquide comprend au moins un monomère photoréactionnel et au moins un photoamorceur, caractérisée en ce que la composition de résine durcissable par rayonnement comprend 50 à 80% en poids d'une charge, par rapport au poids total de la composition.
2. Composition de résine durcissable par rayonnement selon la revendication 1, dans laquelle le constituant liquide de la composition de résine est formulé à partir des composants comprenant :
 - (A) 30 à 95 % en poids d'un composé polymérisable cationique ;
 - (B) 0,1 à 10% en poids d'un amorceur de photopolymérisation cationique ;
 - (C) 5 à 30% en poids d'un monomère éthyléniquement insaturé ;
 - (D) 0,01 à 10% en poids d'un amorceur de photopolymérisation radicalairedans laquelle les quantités des composants du constituant liquide de la composition s'additionnent jusqu'à 100% en poids.
3. Composition de résine durcissable par rayonnement selon l'une quelconque des revendications 1 et 2, dans laquelle le constituant liquide comprend un composé polymérisable cationique composé de 50% en poids ou plus d'un composé contenant un époxy.
4. Composition de résine durcissable par rayonnement selon l'une quelconque des revendications 1 à 3, dans laquelle le constituant liquide comprend un composé polymérisable cationique composé de 50% en poids ou plus d'un composé époxy choisi dans le groupe formé par le carboxylate de 3,4-époxycyclohexylméthyl-3',4'-époxycyclohexane et le bis(3,4-époxycyclohexylméthyl)adipate.
5. Composition de résine durcissable par rayonnement selon l'une quelconque des revendications 1 à 4, dans laquelle le constituant liquide comprend un composant monomère éthyléniquement insaturé comprenant au moins 60% en poids d'un monomère polyfonctionnel ayant au moins trois liaisons éthyléniquement insaturées dans la molécule.
6. Composition de résine durcissable par rayonnement selon l'une quelconque des revendications 1 à 5, dans laquelle ladite charge est choisie dans le groupe formé par les charges organiques, les charges inorganiques ou un mélange de charges inorganiques et organiques.
7. Composition de résine durcissable par rayonnement selon l'une quelconque des revendications 1 à 5, dans laquelle la charge est un composé organique choisi dans le groupe formé par une ou des résines, un ou des caoutchoucs ou un mélange d'une ou de résines et d'un ou de caoutchoucs.
8. Composition de résine durcissable par rayonnement selon l'une quelconque des revendications 1 à 6, dans laquelle ladite charge est une poudre ayant des particules sphériques.
9. Composition de résine durcissable par rayonnement selon l'une quelconque des revendications 1 à 6, dans laquelle la charge inorganique est choisie dans le groupe formé par la silice fondue, la silice cristalline ou un mélange de silice fondue et de silice cristalline.
10. Composition de résine durcissable par rayonnement selon l'une quelconque des revendications 1 à 5, dans laquelle ladite charge est une poudre de silice ayant une granulométrie moyenne ou une longueur de fibre de 1 à 50 µm.
11. Composition de résine durcissable par rayonnement selon l'une quelconque des revendications 9 et 10, dans laquelle ladite charge est traitée avec un agent de couplage silane.
12. Composition de résine durcissable par rayonnement selon l'une quelconque des revendications 9 à 11, dans laquelle ladite composition comprend de plus un agent de couplage silane.
13. Procédé pour fabriquer un moule en vue de fabriquer des produits à partir de matières fibreuses en réalisant une combinaison d'étapes consistant à :

(1) appliquer une couche mince d'une composition de résine durcissable par rayonnement sur un plateau support ;

(2) irradier sélectivement la couche mince de résine de façon à durcir une partie choisie de ladite résine ;

(3) appliquer une couche mince supplémentaire de résine ;

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et répéter les étapes (2) et (3) de façon à obtenir une forme tridimensionnelle d'une pluralité de couches durcies, **caractérisé en ce que** la composition de résine, comme définie selon l'une quelconque des revendications 1 à 12, est utilisée.

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14. Moule pour fabriquer des produits à partir de matières fibreuses susceptible d'être obtenues par un procédé selon la revendication 13.

15. Moule selon la revendication 14, dans lequel le moule contient des trous d'aspiration ayant un diamètre inférieur à 3,6 mm.

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16. Moule selon l'une quelconque des revendications 14 et 15, dans lequel le moule possède un indice d'égouttage d'environ 400 à 600 ml (selon la norme JIS 8121).

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17. Procédé pour fabriquer des produits à partir de matières fibreuses en utilisant un moule selon l'une quelconque des revendications 13 à 16, dans lequel le moule est mis en contact avec une suspension de pâte à papier brute, en réduisant la pression à l'intérieur du moule pour fabriquer une préforme pâte à papier-fibre qui est ensuite séchée et éventuellement durcie de façon à obtenir un produit de pâte à papier moulée.

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FIG. 1

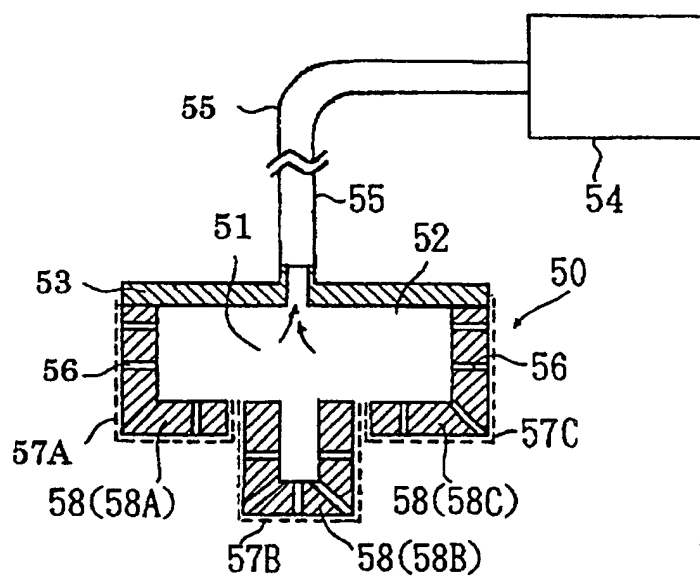


FIG. 2

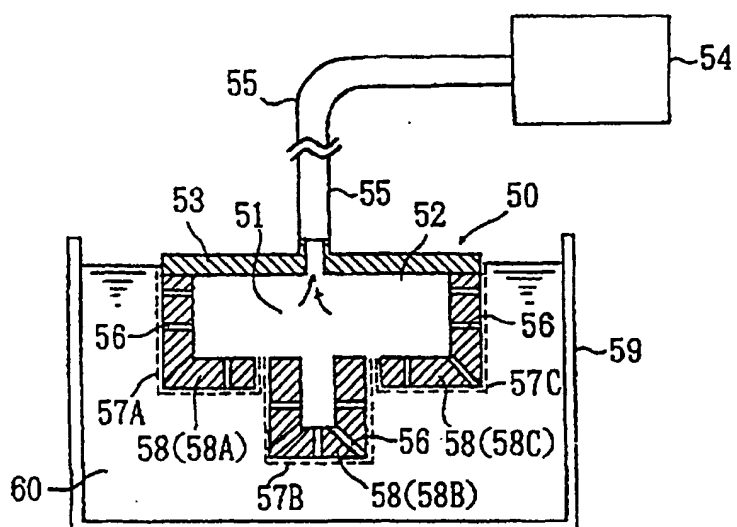


FIG. 3

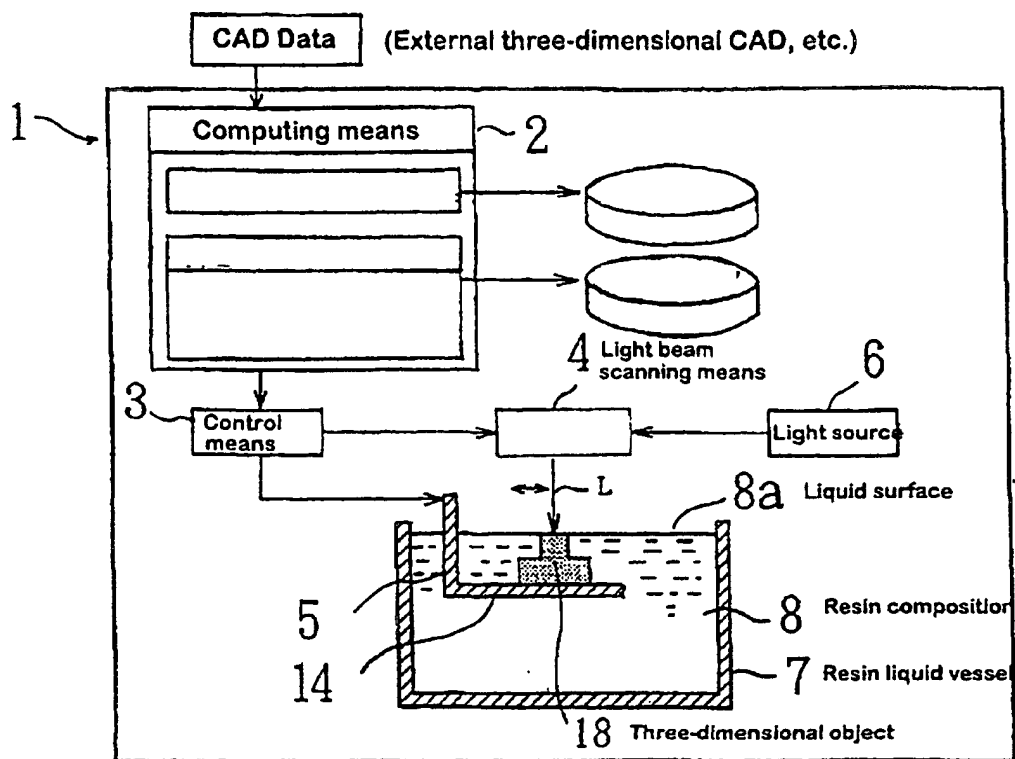


FIG. 4

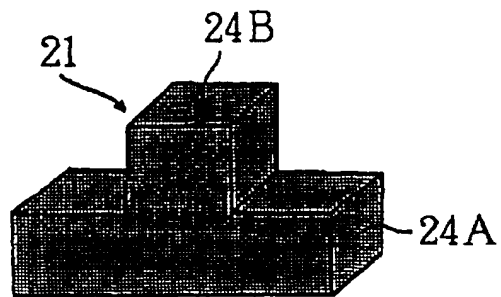
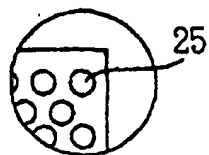
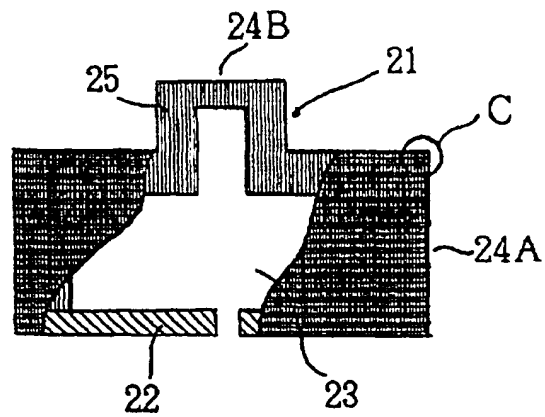


FIG. 5



Details of part C